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POTENTIAL FOR HIGH TEMPERATURE SUPERCONDUCTIVITY

D. C. Reynolds
Y. Chung
S. B. Nam

Electronic Research Branch
Electronic Technology Division

July 1982

Final Report for Period April 1980 - October 1981

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DONALD C. REYNOLDS, Project Engineer
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FOR THE COMMANDER

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The investigation of Cu Cl at high pressure revealed magnetic anomalies that were characteristic of a superconducting state. Subsequent to these investigations similar effects were observed in pressure quenched CdS.

These preliminary results were very promising, though considerably more work was required to confirm the mechanism as well as to gain a better understanding of the materials that exhibit the desired properties. In view of these observations an LDF program was initiated, the goal of which was to reproduce some of the magnetic anomalies and to try to understand something of the

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mechanism as well as what properties the materials needed to demonstrate the effect. The initial investigations were very devoted to Cu Cl since more was known about the high temperature diamagnetic anomaly in this material than any other material. Pressure cells were constructed and a variable temperature Dewar was obtained so the magnetic properties could be investigated over a temperature range from room temperature to liquid helium temperature. The necessary equipment was assembled to measure the diamagnetic and paramagnetic susceptibilities. Cu Cl crystals were grown from the melt from the vapor phase and by a flux technique. The first experiments that were done were optical experiments designed to characterize the starting material as well as to obtain information relating to the material properties that might relate to the mechanisms involved. From high resolution emission experiments a center was observed that could be the center from which the superconducting electrons are supplied as predicted by theory. Studies were made on pressure quenched CdS where both diamagnetic and paramagnetic anomalies were observed. A theory was also developed which shows that in a one-dimensional system, a pair of carriers with momentum $q > 2k_F$ can be stable or metastable, depending on K. The pair binding energy has two relative maxima, the usual one at $q = 0$ and a new maxima at a value of $q > 2k_F$.

FOREWORD

This report covers the work performed under LDF 80-001. The objective of this program was to reproduce some of the magnetic anomalies that had been reported in Cu Cl and CdS. A further objective was to determine if possible the material parameters that were important in producing these anomalies. All of the investigations were done on Cu Cl and CdS.

The principal contributors to the program during its existance were the following:

Y. Chung, Principal Investigator

S. B. Nam, Research Scientist

D. C. Reynolds, Research Scientist

This project was supported, in part, by the Laboratory Director's Fund (AFR 80-3).

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SECTION I

POTENTIAL FOR HIGH TEMPERATURE SUPERCONDUCTIVITY

I. INTRODUCTION

This Lab Director's Fund (LDF) program investigates a process by which high temperature superconductivity may be realized. Preliminary experiments have been encouraging and the potential for technological advancement is immense. Additional research could lead to the introduction of a new technology having a tremendous impact on the performance and cost of advanced avionic systems by making possible the execution of electronic functions considered impractical by current techniques.

The phenomenon of superconductivity was discovered by Kamerlingh Onnes in 1911. A reasonable understanding of the phenomenon was not realized until the BCS (Bardeen, Cooper, Schrieffer) theory in 1957. Many of the properties of superconductivity were investigated in the interim period. One of the properties that aided in the final understanding was the relaionship between the critical temperature and the mass of isotopes of the same material:

$$T_c M \; a \approx \text{constant}$$

where $a \approx 1/2$ in a number of cases.

It was clear that the transition from the normal state to the superconducting state was primarily electronic in character in the sense that it is the properties of the electrons that differ in the normal and superconducting states. From this it was concluded that the independent-particle model of conduction electrons would not yield an understanding of superconductivity. The simplest model on which to base a theory would be a collection of interacting electrons. This model runs into difficulty when the energy associates with the various interactions is compared with the energy difference between the normal and superconducting phases, the interaction energies are much too large.

Another model for the interaction responsible for superconductivity is the electron-phonon interaction. The isotope effect indicated that this interaction did indeed play an important role. The theories that followed were based on the diagonal or self-energy part of the electron-phonon interaction which turned out to be the off-diagonal part of the electron-phonon interaction.

The basic processes in which the electron-phonon interaction is manifested are the absorption or emission of a phonon by an electron. The next simplest process would be the emission and subsequent absorption of a phonon by the same electron. These processes are explained by the diagonal part of the electron-phonon interaction. The process by which the electron-phonon interaction leads to an effective electron-electron interaction is the exchange of a phonon between two electrons. The phonons involved in this process are virtual phonons and the coupled state is an intermediate state.

The interaction between electrons via an exchange of virtual phonons can be described classically. When an electron moves through a lattice of positive and negative ions it interacts via the coulomb interaction and thus distorts or polarizes the lattice. A follow-on second electron experiences an interaction not with the unperturbed lattice, but rather with the distorted lattice. One electron affects another with the lattice as the intermediary. The phonon is a quantized lattice vibration, thus the interaction is the phonon mediated electron-electron interaction. The intermediate phonon propogates with a finite speed characteristic of the lattice. Thus the interaction is retarded. For the phonon-mediated interaction to lead to superconductivity it must be strong enough to dominate the residual screened coulomb interaction.

The superconducting phase has lower energy than the normal phase thus the electron-electron interaction can lead to superconductivity only if it is attractive. The interaction becomes attractive through the exchange of virtual phonons.

The excitation exchanged by the electrons must be a boson because the kinematics of the exchange requires it to carry zero or unit spin. Other possibilities arise for the replacement of the phonon by other intermediate bosons. Excitations which might be exchanged by electrons to produce an effective electron-electron interaction includes excitons.

For many years it was thought that superconductors differed from normal conductors only in having zero electrical resistance. In 1933 Meissner and Ochsenfeld found that a solid cylinder of lead or tin situated in a uniform magnetic field expels the magnetic flux as it is cooled from the normal state below its critical temperature to the superconducting state. This effect is now called the Meissner effect. Another significant development in the field was the idea of an energy gap in the superconducting state. The electrons in a metal are distributed in such a way that at any instant of time each electron occupies a discrete energy state. The number of states available for occupation by free electrons is a function of their energy. This is expressed by the density of state curve in which the ordinate represents the number of energy states per unit energy interval In a superconductor the energy gap is a maximum at the absolute zero of temperature and vanishes at the critical temperature. The gap is symmetrical about the Fermi energy. The Fermi energy is defined as the maximum energy level up to which the energy states are completely occupied at absolute zero. The width of the gap Δ is

$$\Delta \sim a\, E_{phonon}$$

where a is the electron-phonon coupling constant and E_{phonon} is the virtual phonon energy

The phenomena of having an exciton mechanism cause superconductivity opens the doors to the ability to have room temperature superconductors. A set of very interesting experiments on Cu Cl reveals that the magnetic susceptibility changes from $\sim -10^{-6}$ to -1, revealing the Meissner effect. Brandt et al.(1) found by cooling Cu Cl with a speed of 20 K/min under a hydrostatic pressure of 5 K bars that at ~170 K a series of transitions from the state of weak diamagnetism to that of a state of strong diamagnetism ($\chi \sim -1$) occurred. The strong diamagnetic state was accompanied by a

sharp increase in electrical conductivity. Similar experiments under controlled environment were also performed by Chu et al[2]. They found the diamagnetic anomaly above 90 K over a temperature range of 10-20 K in the AC magnetic susceptibility along with a sharp increase in the electrical conductivity. The results are shown in Figs. 1 and 2.

To explain the above experiments, Kunz and Collins[3] calculated band structure of Cu Cl which is shown in Fig. 3. The effect of a smal amount of pressure makes the conduction band minimum at Γ become degen ate with the Conduction band minimum at X. Another important point is that a fair amount of oxygen is present in all of the Cu Cl samples. The calculations reveal that the energy of the O bound electron is less than the binding energy of the exciton and will give up part of its electrons to the conduction band at the experimental temperatures. An upper limit on the critical temperature of an electron-exciton coupled superconductor can be obtained assuming the static limit of the coupling of the electron and exciton and assuming the T_C can be approximated by:

$$T_C = 1.14 \frac{h\,\omega_{ex}}{K_B} \exp\left[-1/\nu\, D_{(\epsilon f)}\right]$$

where T_C is the superconducting transition temperature; ω_{ex} is the energy of the exciton; ν is the coupling coefficient of the electron and exciton; and $D_{(\epsilon f)}$ is the density of electrons at the Fermi surface. The results are given in Fig. 4. Considering only the Γ point conduction band minimum with 10% impurities the transition temperature is 38 K, however, when the X-band minimum is included one gets a T_C = 1745 K. This explains the effect of pressure in producing the anomalous (superconducting) state in Cu Cl.

We recall that the superconducting band gap in phonon coupled superconductors was expressed as

$$\Delta \simeq a\, E_{phonon}$$

where a is the coupling coefficient and E_{phonon} is the phonon energy. The gap energy for this case is ~10^{-3} to 10^{-4} eV. In the case of exciton coupled superconductivity the superconducting gap is expressed as:

$$\Delta \simeq a\, E_{ex}$$

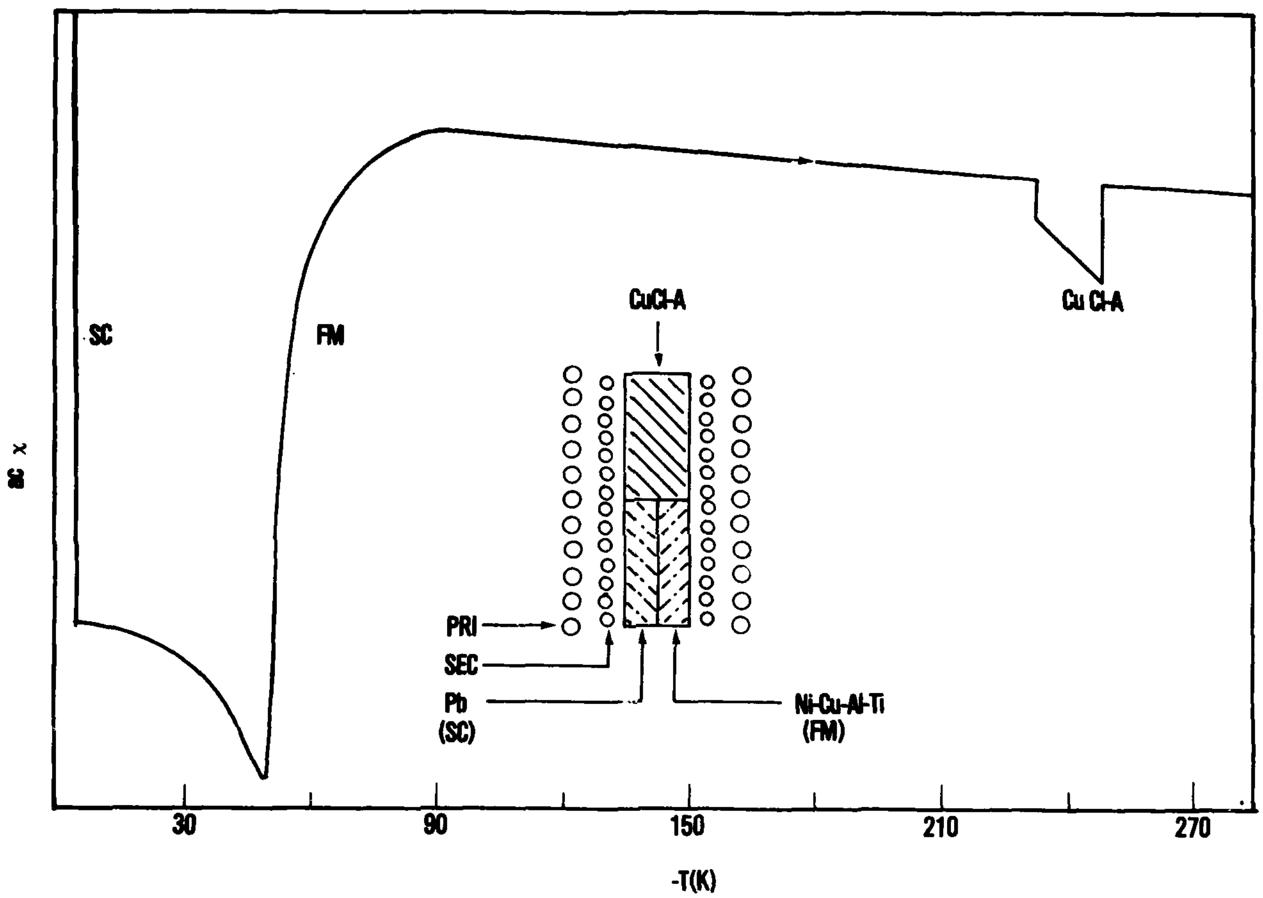

Fig. 1. The schematic temperature dependence of χ of a rapidly warming Cu Cl sample, a superconducting Pb and a ferromagnet $Cu_{66}NI_{29}Al_3Ti_2$. It should be noted that the sample coil and the coil around the superconductor and the ferromagnet were oppositely connected to each other. The strong temperature dependence of χ between 7 and 50 K is attributed to the skin effect of Pb and the magnetic signal of the ferromagnet.

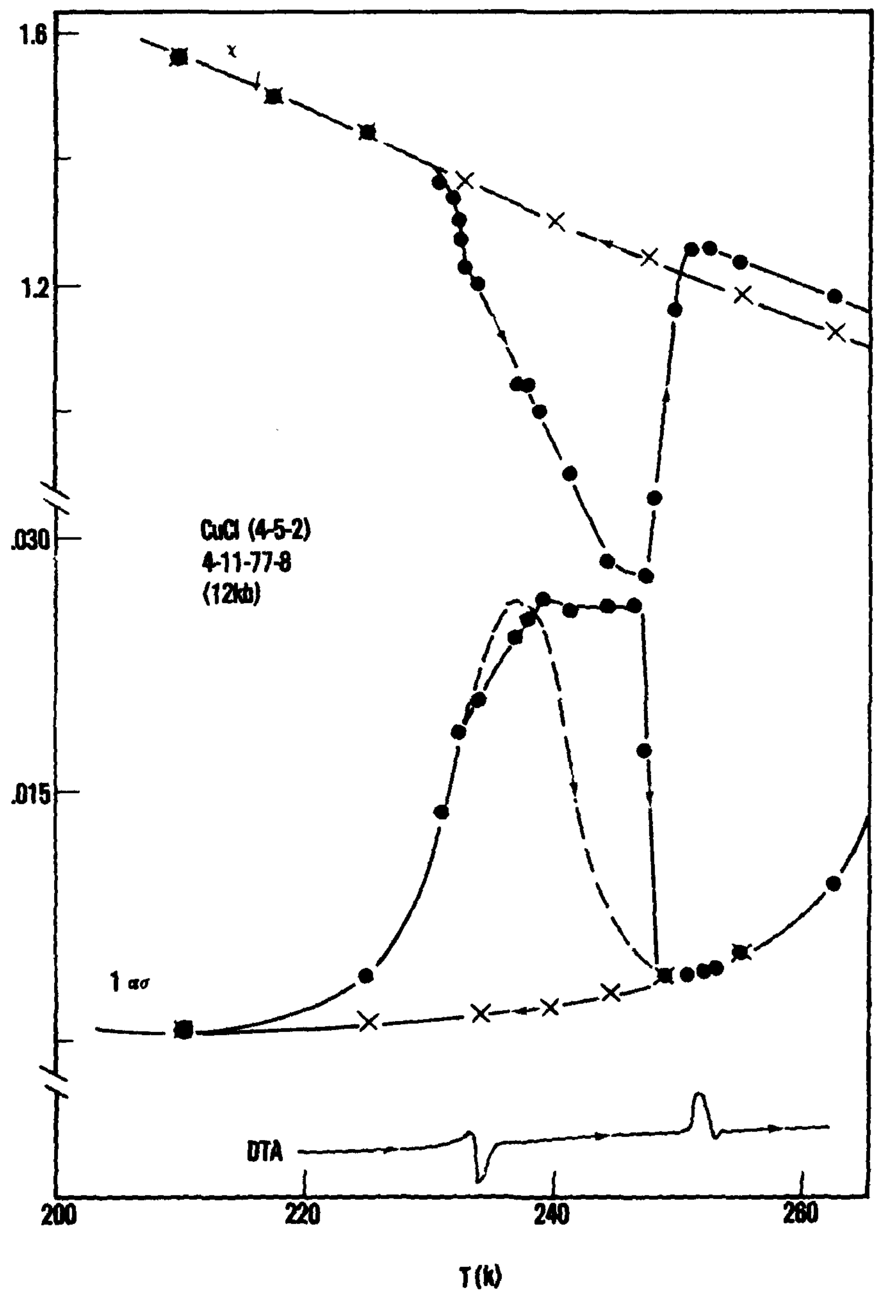

Fig. 2. *The χ-, I- and anomalies of Cu Cl. I was the current flowing* through the sample *and* therefore a measure of σ of the sample. The dashed curve represented the expected due to the detrapping of charges by thermal excitation.

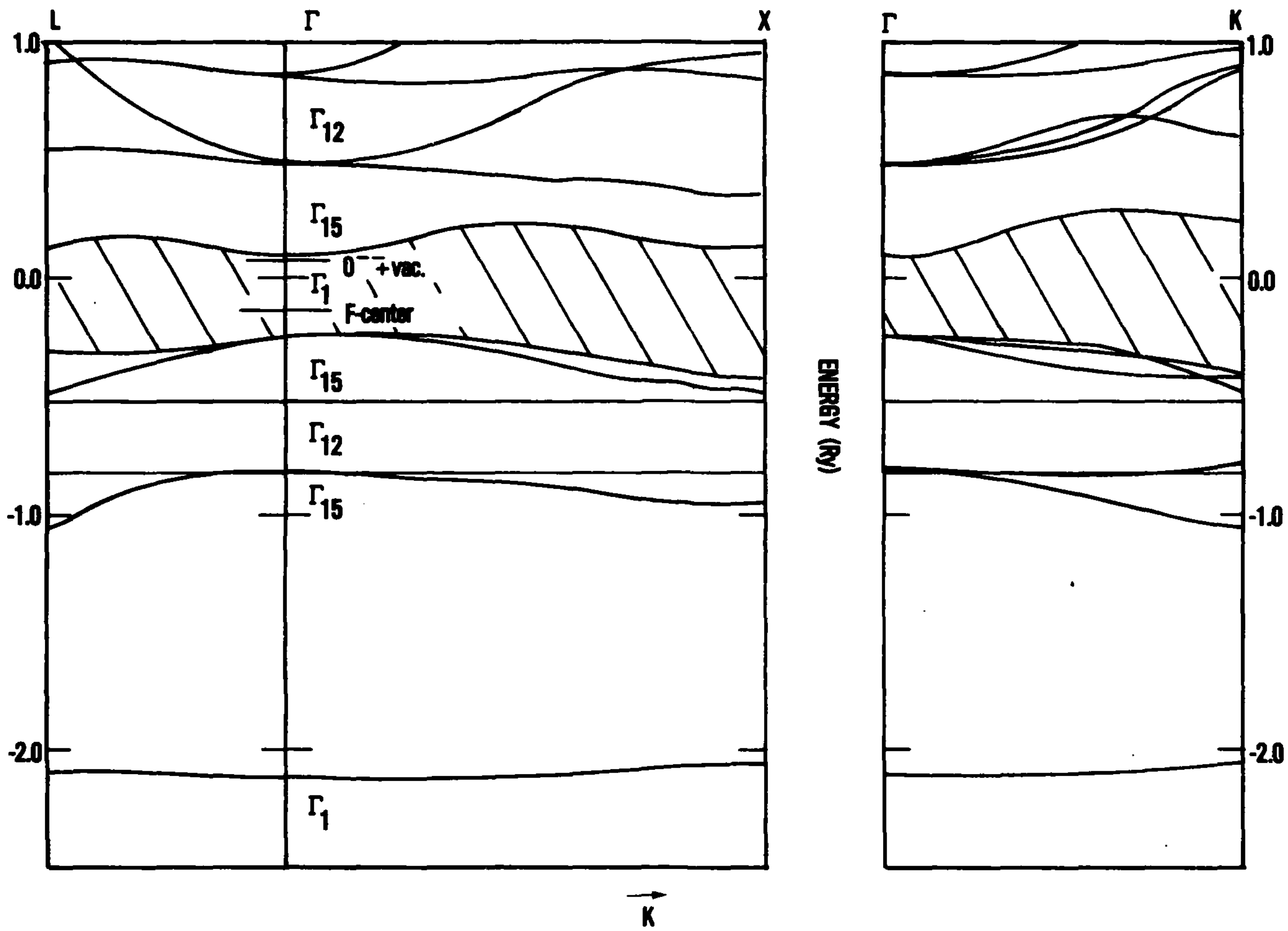

Fig. 3a. Cu Cl band structure. The maximum of the valence band is at Γ (mostly Cu 38) and the minimum of the conduction band is also at Γ (mostly Cu 45) the O^{--} impurity state is very near the bottom of the conduction band and is bound less than the exciton binding energy.

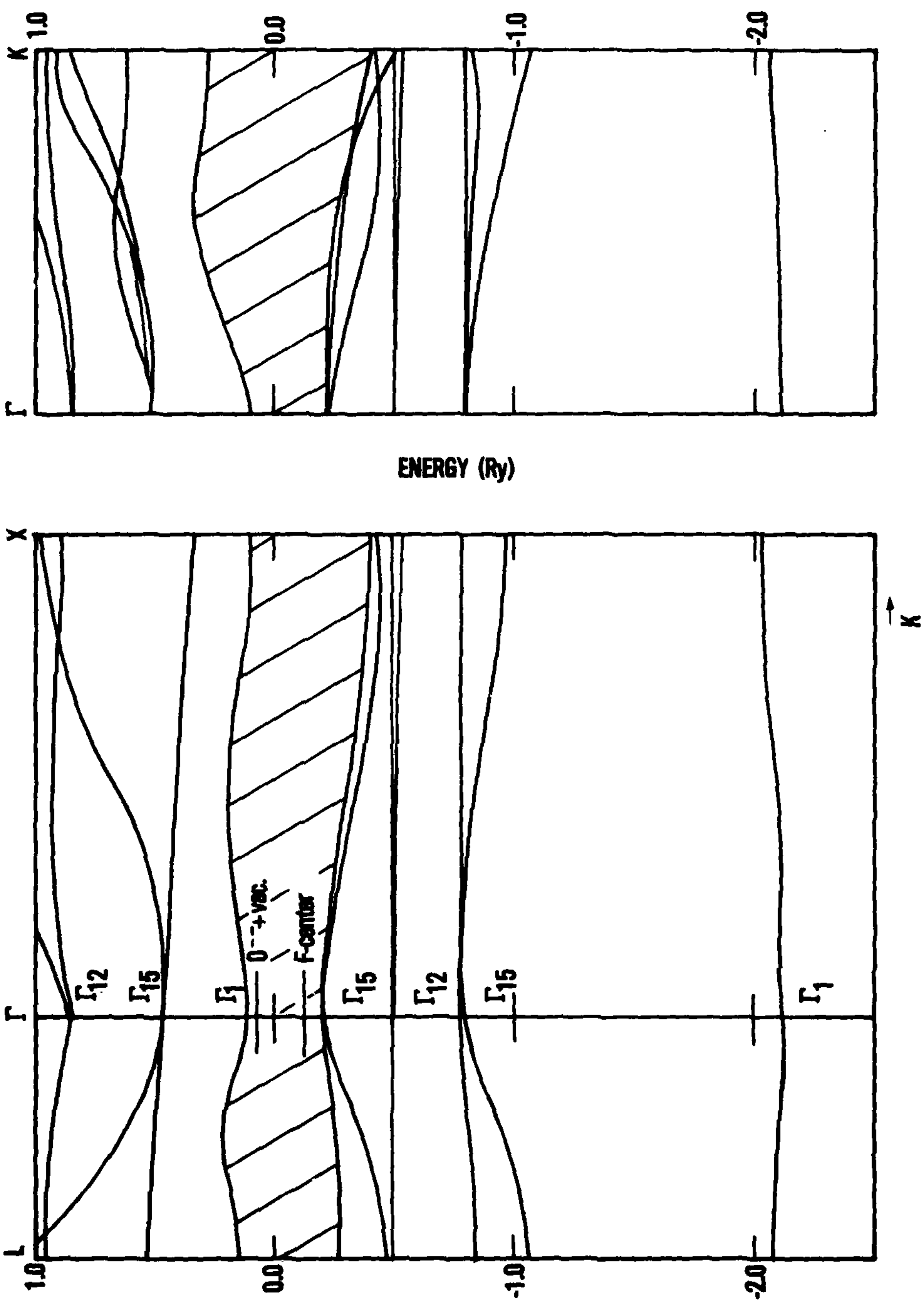

Fig. 3b. Cu Cl band structure with 0.99 x (*Lattice Constant*) to represent pressure effects. The maximum of the valence band is at Γ and the minimum of the conduction band is at X. This causes the density of states at the Fermi Surface to increase more than an order of magnitude.

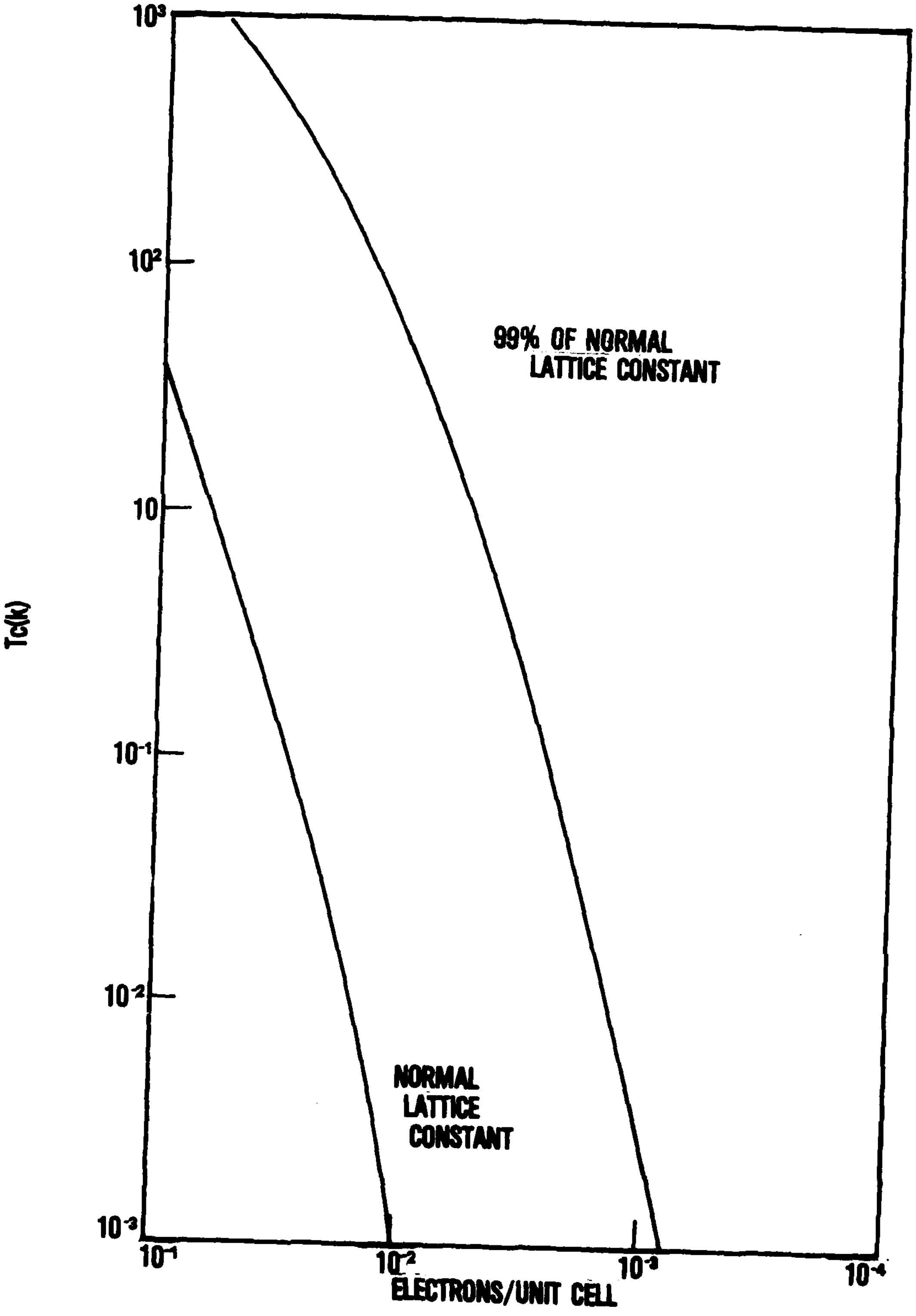

Fig. 4. The approximate T_c of the Cu Cl as a function of concentration of oxygen. The normal a curve is the T_c curve without pressure and 99% of a curve is the effect of a small amount of pressure on T_c. The approximate expression does not include the screening effects of the conduction electrons on themselves.

where again a is the coupling coefficient, but E_{ex} is now the exciton energy. In Cu Cl the exciton energy is greater than 3 eV. Phonon energies are of the order of a few millivolts, which illustrates the feasibility for high temperature superconductors in exciton coupled materials.

Shortly after the magnetic anomalies were observed in Cu Cl, similar effects were observed in pressure quenched CdS.(4)

These preliminary results were very promising, though considerably more work was required to confirm the mechanism as well as to gain a better understanding of the materials that exhibit the desired properties. In view of these observations an LDF program was initiated, the goal of which was to reproduce some of the magnetic anomalies and to try to understand something of the mechanism as well as what properties the materials needed to demonstrate the effect. The initial investigations were devoted to Cu Cl since more was known about the high temperature diamagnetic anomaly in this material than any other material. Pressure cells were constructed and a variable temperature Dewar was obtained so the magnetic properties could be investigated over a temperature range from room temperature to liquid helium temperature. The necessary equipment was assembled to measure the diamagnetic and paramagnetic susceptibilities. Cu Cl crystals were grown from the melt from the vapor phase and by a flux technique. The first experiments that were done were optical experiments designed to characterize the starting material as well as to obtain information relating to the material properties that might relate to the mechanisms involved. From high resolution emission experiments a center was observed that could be the center from which the superconducting electrons are supplies as predicted by the theory of Kunz and Collins.(3)

SECTION II

DONOR-ACCEPTOR RECOMBINATION SPECTRA IN Cu Cl

Recently, a series of very interesting experiments on Cu Cl have revealed that the magnitude of its magnetic susceptibility varies over a wide range, from $\sim -10^{-6}$ to -1, under controlled experimental conditions.

Although still a conjecture, there is nevertheless a strong possibility that Cu Cl, and related materials, may be capable of supporting a supercurrent at elevated temperatures and pressures. These experiments have stimulated a renewed interest in Cu Cl, its electrical and optical properties, and its energy band structure. The energy band structure of Cu Cl has been recently calculated by Kunz and Collins[(3)] which included a theoretical study of possible defect and or impurity levels. These calculations have predicted an O^{--} bound-electron level lying near to the conduction band minimum. It is this level which is speculated to be the source of electrons for the highly conducting state. The present investigation describes the first observation of donor-acceptor pair spectra in Cu Cl. It will be shown that one component of the donor-acceptor pairs must be doubly charged, a characteristic which would be compatible with the O^{--} center.

The samples employed were water-clear single crystals grown from the vapor phase, by a technique similar to that of Chu et al.[(2)] Photoluminescence was excited with a high-pressure Hg-lamp at sample temperatures <2 K. Spectral analysis of the luminescence was provided by a high-resolution, high-dispersion spectrograph (~1 A/mm) which employed photographic recording of the spectral data. Zeeman splittings of the spectral lines were produced by magnetic fields up to 40 kG, with the samples oriented in the Voigt configuration ($q \perp H$).

Photoluminescence spectra were analyzed from three samples as well as from different parts of the same sample. Some of the emission lines were common to all samples while others were uniquely observed in a particular sample. More than 60 lines have been observed in the energy

region 3.111 16-3.203 47 eV. Shown in Fig. 5 is a typical spectrum, a section of which has been expanded (between 3.158 71 and 3.203 47 eV) to more clearly illustrate some of the details. The line at 3.180 10 eV is a bound-exciton line previously reported by Certier, Wecker, and Nikitine.[5] All of the pair lines were characterized by a four-component magnetic field splitting, and polarization data showed that the low- and high-energy components were π lines. A geometrical construction of the magnetically split components of the line at 3.162 34 eV is illustrated in Fig. 8. The splitting is typical of the magnetic field behavior of all of the pair lines although the magnitude of this splitting does vary somewhat from line to line.

From the magnetic-field data a number of conclusions can be drawn. Cu Cl crystallizes in the zinc-blende structure which is common to many II-VI and III-V compounds. In virtually all such materials, the top valence band is of Γ_8 symmetry while the lower valence band is of Γ_7 symmetry. Cu Cl, on the other hand, is characterized by a negative spin-orbit splitting, as a result of a mixing of Cu d electrons overlapping with the Cl p potential sites. This interaction reverses the valence band ordering, putting the Γ_7 band highest, which is reflected in the four-component splitting, and also in the four-component splitting of the bound exciton reported by Certier, Wecker, and Nikitine.[5]

From the Γ_6 conduction band and the Γ_7 valence band a triply degenerate Γ_5 transition and a singly degenerate Γ_2 transition are possible. Assume that the pairs are made up of simple donors and acceptors, in which case the upper state will consist of a J=1 and a J=0 state, depending on the orientation of the spins, and the lower state will always be a singlet, as shown in Fig. 7. For this simple donor-acceptor complex, one would expect to observe a zero-field splitting due to the exchange interactio between the electron and hole spins; this is not observed experimentally. In the presence of an external magnetic field, the J=1 state will split into three components while the J=0 state will not split. The optical transitions from this magnetic-field-split configuration result in a low-energy σ line and a high-energy σ line, with the intermediate-energy lines being π lines. Just the opposite is

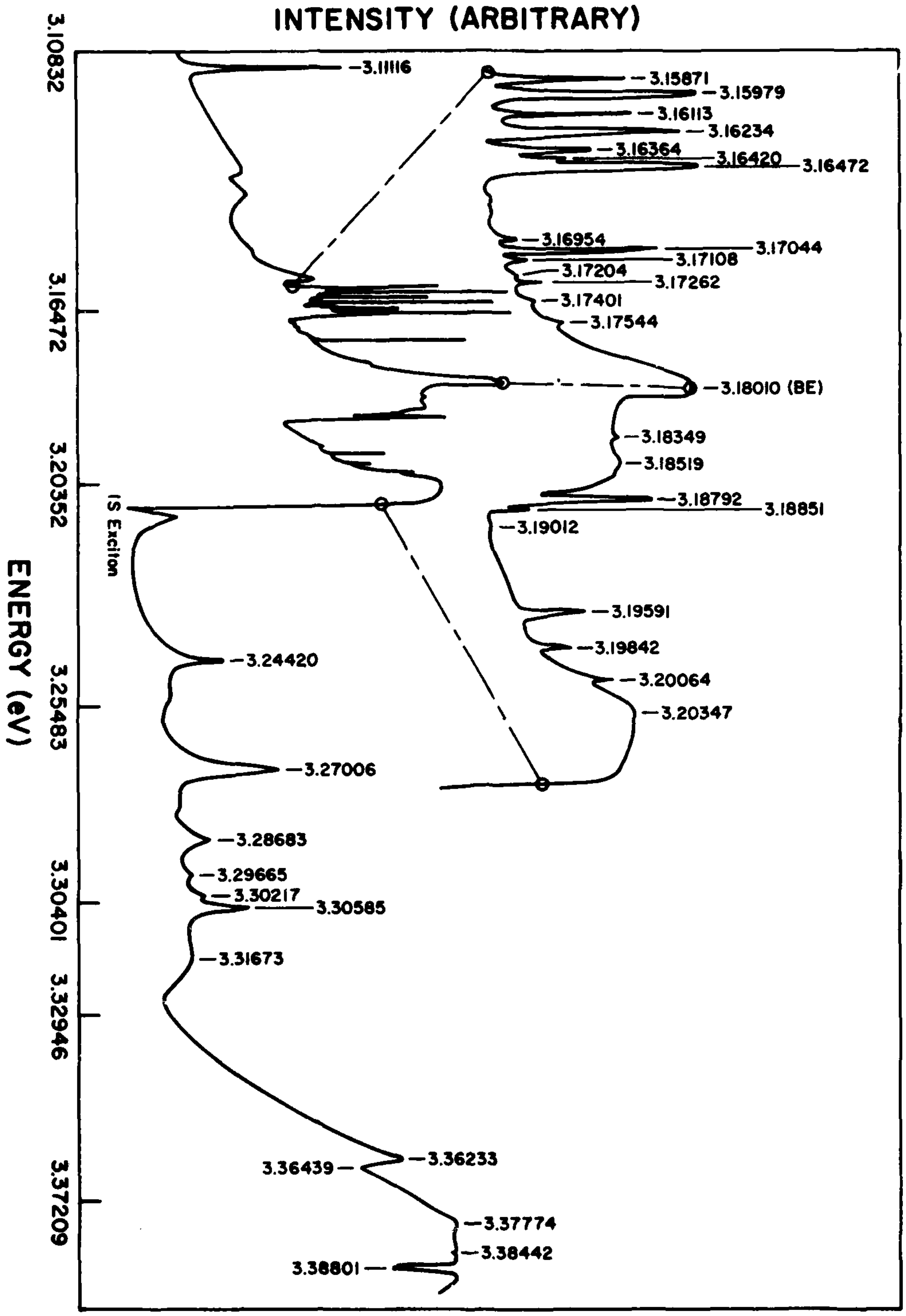

Fig. 5. Photoluminescence spectra showing donor-acceptor pair recombination in Cu Cl. Expanded scale shows spectra in greater detail.

observed experimentally. Thus, the simple donor-acceptor model can be ruled out because of the absence of an exchange splitting and the observed polarization which is not compatible with the simple model.

Consider now another type of donor-acceptor complex, one in which the donor is doubly charged, as diagrammed in Fig. 6. With such a model it is possible to account for all of the experimental data. In the upper state the two electron spins will pair leaving an unpaired $J=1/2$ unpaired electron state. Moreover, in the presence of an applied magnetic field, both the upper and lower states will split as doublets, accounting for the observed four-component splitting of the spectral lines. In order that the low-energy component and the high-energy component be π lines it is necessary that either the electron g value or the effective hole g value (K) be negative. It has already been shown by Certier, Wecker, and Nikitine[5] that the hold g value in Cu Cl is negative. Thus, the data are consistent with previous observations. For the line shown in Fig. 2, an electron g value $g_e = 1.73$ and a hole g value $K = -1.32$ were calculated. Donor-acceptor pair spectra are frequently characterized by a convergence limit which implies that the pairs are randomly distributed throughout the lattice. The absence of such a limit indicates a nonrandom distribution of the pairs, which is not uncommon. For example, Henry, Nassau, and Shiever[6] observed a nonrandom double donor-acceptor pair distribution in CdS and Reynolds, Litton, and Collins[7] observed a nonrandom double acceptor-donor pair distribution in the same material.

An analysis for oxygen was performed on one of the Cu Cl samples by means of Auger-electron spectroscopy (AES) according to the following procedures. Variation of the O content from the surface to the interior of the sample was determined by sputtering away the Cu Cl over a 1-mm-diameter spot to a depth of 15 μm and periodically monitoring the first-derivative Auger spectra of the sputtered area. The sputtering was carried out at relatively high energy and rates over a period of several hours in an ultrahigh-vacuum system ($1X10^{-10}$ Torr base pressure) back-filled with high purity argon to total pressure of $4X10^{-5}$ Torr. In addition to Cl and Cu in approximately stoichiometric proportions, presputter

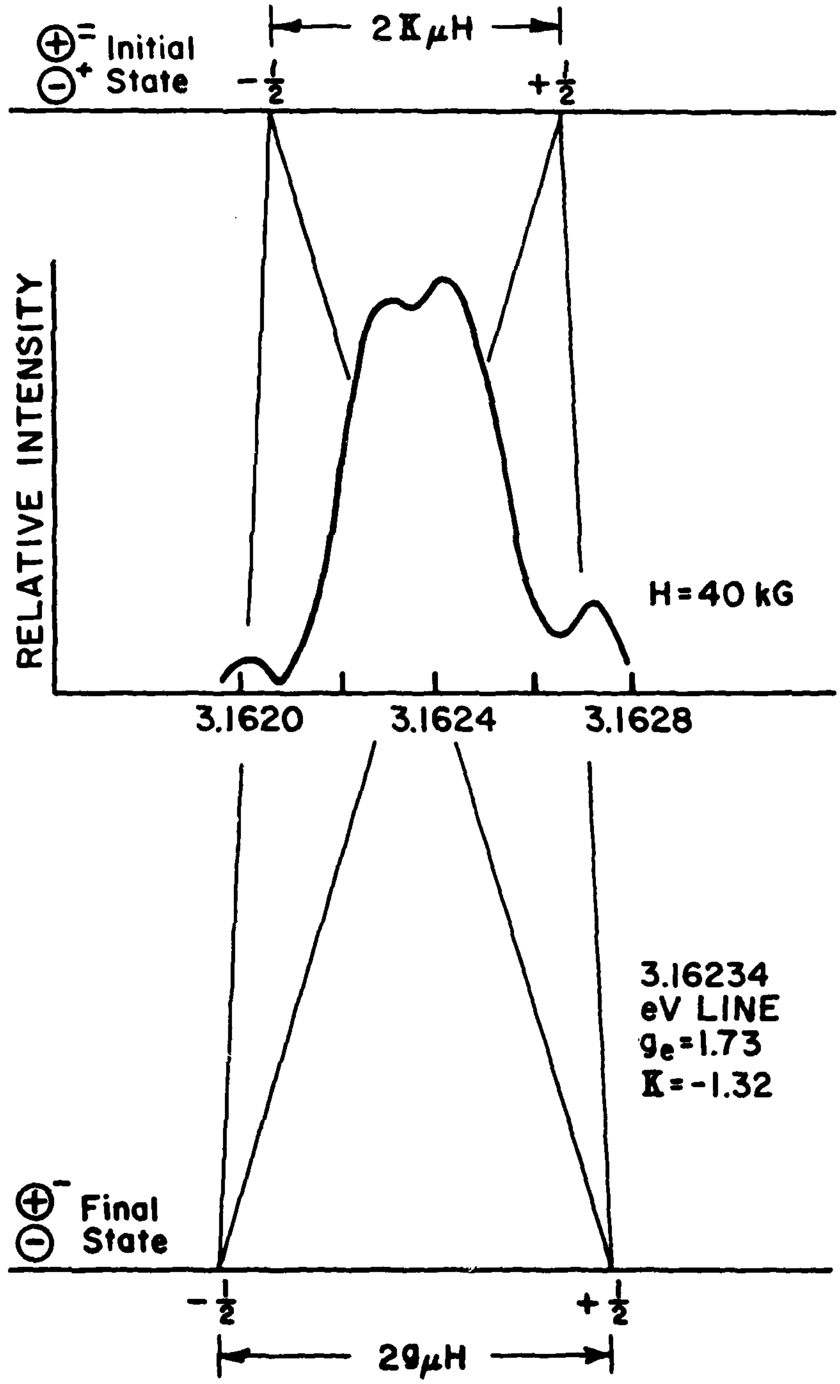

Fig. 6. Transition nomogram showing behavior of 3.162 34-eV line in applied 40-kG magnetic field. The field-split lines are shown for the polarization E $\perp$ H in which the σ lines are allowed. G_e = 1.73; K = -1.32.

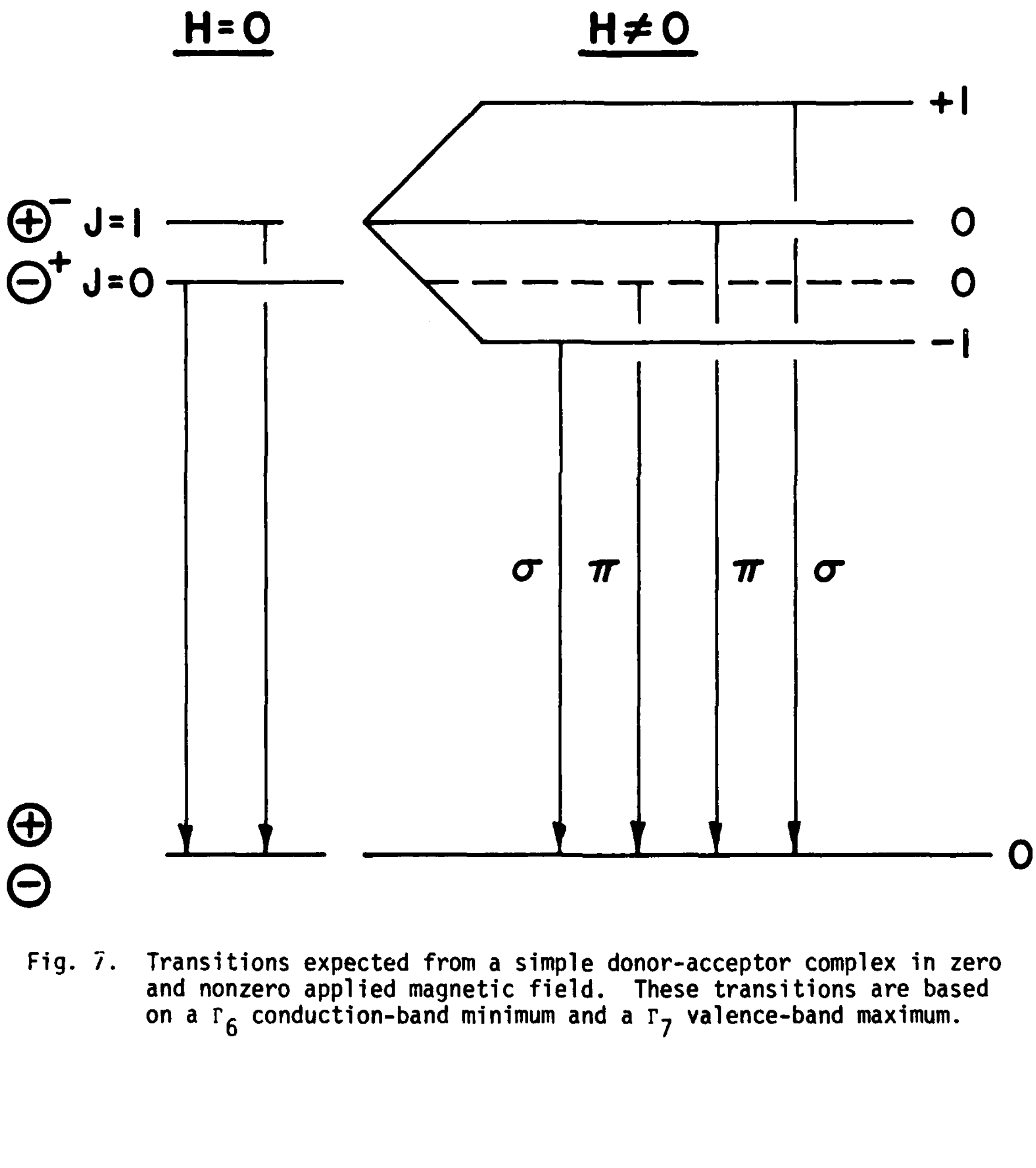

Fig. 7. Transitions expected from a simple donor-acceptor complex in zero and nonzero applied magnetic field. These transitions are based on a Γ_6 conduction-band minimum and a Γ_7 valence-band maximum.

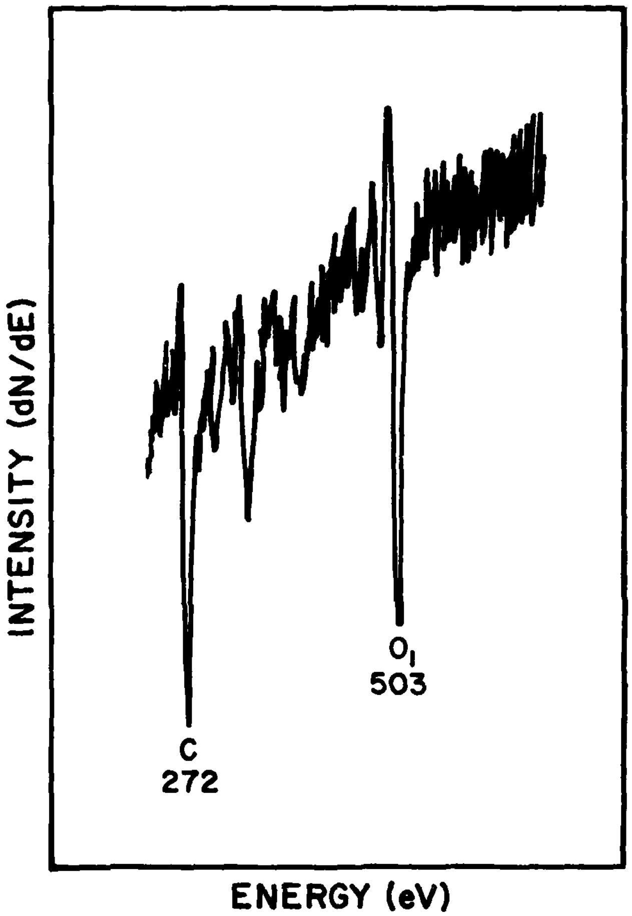

Fig. 8. First-derivative Auger spectrum of a Cu Cl photoluminescence sample taken under high-gain conditions at a depth of 10 μm from the surface.

AES surface scans showed relatively weak KLL transitions of approximately equal strengths at 272, 379 and 503 eV, indicating the presence of surface-absorbed C, N, and O, respectively. The surface layer was removed by low-energy sputter cleaning procedures. However, after sputtering away only a few nanometers, AES scans over the range 0-2000 eV (5-keV beams energy) showed extremely weak O(503) and C(272) peaks, an observation which persisted to a depth of approximately 10 μm. Typical of these scans is the high-gain spectrum shown in Fig. 8 accentuating the energy range of O and C. By the time 15 μm of sample was sputtered away, O was below the detection limit of the spectrometer, $\sim 1 \times 10^{19}/cm^3$. Crude calculations indicate that the O concentration within the first 10 μm of sample depth was very high, between 8×10^{18} and $2 \times 10^{19}/cm^3$. Thus, the Auger results clearly confirm that O was present at high concentrations within the sample volume excited for photoluminescence.

The available data are not sufficient to confirm the presence of doubly charge O, nor to confirm that the O^{--} level predicted by Kunz and Collins[3] is one component of the observed donor-acceptor complex, but the photoluminescence data are consistent with the O^{--} center being one component of the complex. It is recognized that other chemical species or host defects may give rise to the observed pair spectra and thus cannot be ruled out at this time. It is clear, nevertheless, that one component of the complex must be doubly charged in order to explain the data. It is further clear from these data that electron donors play a nonnegligible role in the properties of Cu Cl and may well be in part responsible for the observed diamagnetic anomaly.

SECTION III

MAGNETIC ANOMALIES IN CdS

In the case of Cu Cl it is necessary to measure the magnetic properties while the pressure is applied. This requires that the pick up coils be mounted outside the pressure cell. After several experiments it was decided that the equipment was not sensitive enough to detect the magnetic susceptibility signal in this configuration. It was then decided to make similar investigations on CdS where similar magnetic susceptibility anomalies had been observed as reported by Homan and MacCrone[8] and by Homan, Kendall and MacCrone[9]. The effect is observed in pressure quenched CdS meaning that the material is pressurized to approximately 40 K bar and then the pressure is quenched. The sample is then removed from the pressure cell permitting the magnetic measurements to be made on the sample separated from the pressure cell. Experiments of this type were carried out on different sources of CdS. The starting materials were pure, doped (probably Li or others) CdS grown in this laboratory by vapor phase deposition approximately 15 years ago, and also CdS powder from Alpha Inorganics stock no. 20130.

The high pressure bomb of Drickamer's configuration[10] whose chamber was 3/16 in. dia. by 1/8 in. was pressurized by a standard Sheffer HH Series 2000 hydraulic cylinder, or a Carver laboratory press of 3" dia. ram. For the pressure transmitting fluids, NaCl and AgCl were used, and BeCu was used for the gasket. The pressure on the sample was not calibrated, but estimated to be of the order of ~40 K bar. The pressure was released simply by opening the pressure oil valve. The rate of pressure release was not known. For pressure quenching at 77 K, the pressure was released after the pressure bomb was immersed in liquid nitrogen, and the bomb was disassembled. The pressure quenched samples have various colors, orange, red, and black sheen, in contrast to the starting yellow. In Fig. 9 the x-ray test shows that the pieces of black sheen samples have been transformed from the starting hexagonal-wurzite to cubic structures, on the other hand, the pieces of orange red samples are retained in the hexagonal structure.

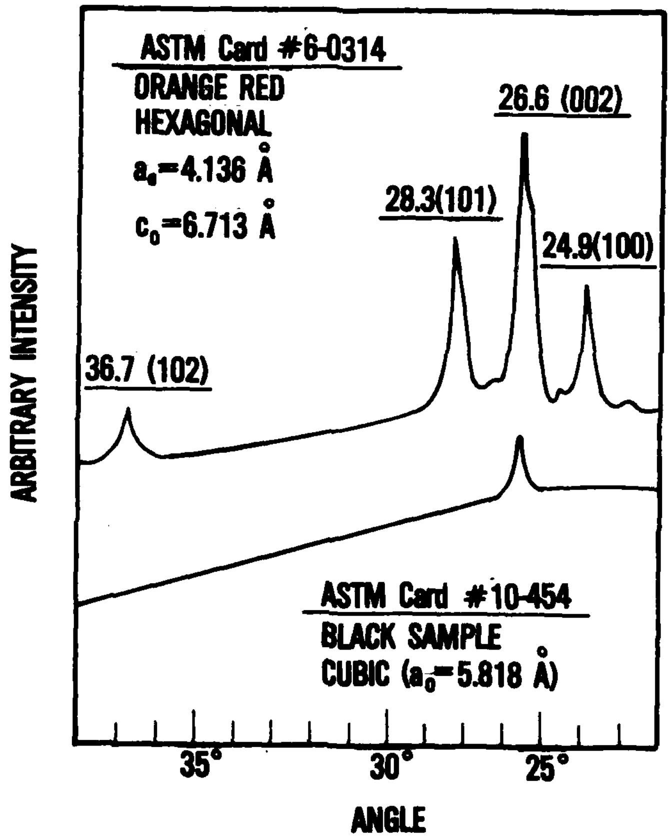

Fig. 9. X-ray analysis of pressure quenched samples.

The measurement of the ac (33 Hz) magnetic susceptibility of the samples was carried out by using pick up coils and a lock-in amplifier PAR model 124A. The reference signal was detected from a 20 Ω resistance connected in series with the primary coil. The inductive part of the signal from the secondary coil was chosen to correspond to the real part of magnetic susceptibility of the sample. All data were taken after the pick up coils and the samples were immersed in liquid nitrogen. For the calibration of susceptibility, a 7 mg sample of $MnCl_2$ was used, whose susceptibility is $\chi = 0.0143$ cgs.

Three of the 25 pressure quenched samples turned out to be diamagnetic with $\chi_v \simeq -1/4\pi \times (0.1 \sim 0.2)$ cgs, and 8 to be paramagnetic with $\chi_v \simeq +0.07$ cgs. The magnetizations of samples disappeared after a few days. We were not able to find any correlation between the starting materials and the quenching temperatures of the magnetized samples. In particular, one sample indicates the transition from the diamagnetic to the paramagnetic states as shown in Fig. 10.

The starting material of this sample was CdS powder from Alpha Inorganics stock no. 20130, and was pressed several times in the pressure range from 30 to 50 k bar, at room temperature. The sample was immersed in liquid nitrogen first, and then transferred into the pick up coils, it appeared to be diamagnetic as AB in Fig. 9, and after a certain period, it became paramagnetic (CD). When the sample was removed from the coils, the signal disappeared (EF), and the sample was put back into the pick up coils, then the same signal reappeared (GH). Thus we believe that the signal indeed came from the sample. We repeated the test several times with this sample, and obtained the similar signal except for the time lapse of BC in Fig. 10. After two days or so, the magnetic properties of this sample disappeared.

We have been able to prepare pressure quenched CdS in both strongly diamagnetic and paramagnetic states. However, we cannot predict in advance whether a specific sample will show unusual magnetic properties after quenching. We did not measure resistivity of the samples. Whether

the system is superconducting or results from macroscopic quantum states requires further investigation.

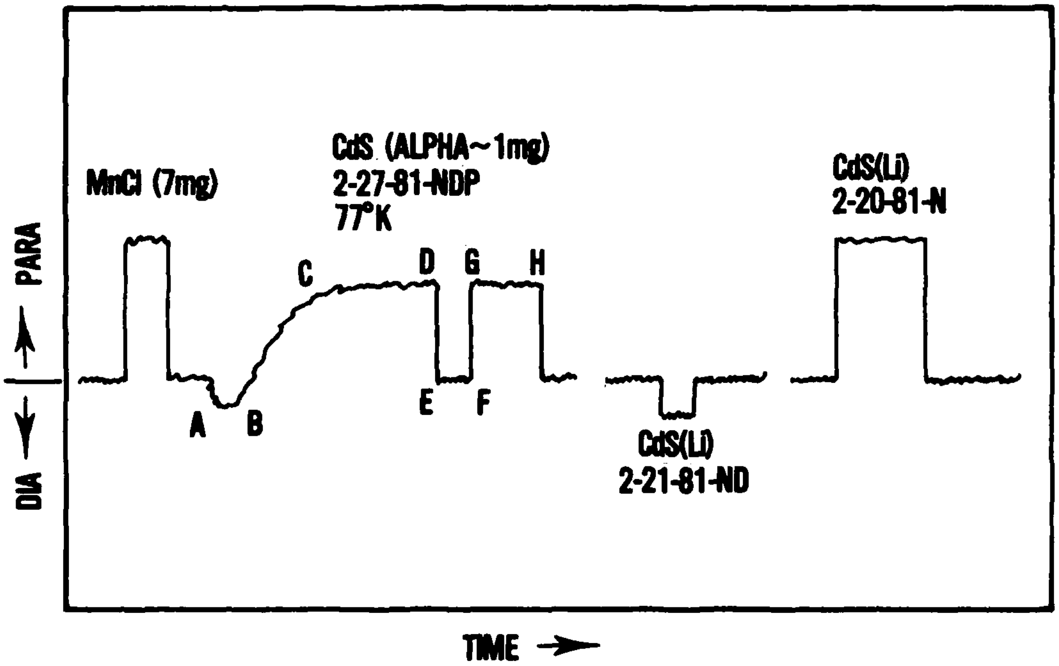

Fig. 10. Dia- and paramagnetic susceptibilities of pressure quenched samples.

SECTION IV

STABILITY OF FINITE MOMENTUM PAIRS IN DEGENERATE FERMI SYSTEMS

A theory was developed by Nam and Allender[11] which shows that in a one-dimensional system, a pair of carriers with momentum of $q > 2k_F$ can be stable, or metastable depending on k_F. The pair binding energy has two relative maxima, the usual one of q=0 and a new maxima at a value of $q > 2k_F$. In a three-dimensional system, it is found that pairs with $q > 2k_F$ can have finite binding energies when the cut-off energy is large.

The complex magnetic properties observed in high pressure quenched CdS have raised much speculation about the possibility of high temperature superconductivity. However, the magnetic states appear to be metastable. The life time of the diamagnetic state is observed to be a few days or so, and that of the paramagnetic state is somewhat longer. This indicates that the states involved are not associated with the true ground state but rather with excited states, or metastable states.

Nam[12] has suggested that pair states of finite momentum involving one, or two component carriers, might be associated with the metastable states. Also hybridized states mixing finite momentum states with a charge density wave might be important. We do believe that for one component carrier, the lowest energy state would be the zero-momentum pairing state of the BCS theory[13]. However, for two component carriers, one might have the lowest energy state occurring for finite momentum pairs[14].

To understand the states of pairs having finite momentum, q, it is desirable to calculate the binding energy of such a pair, in particular when $q > 2k_F$, where k_F is the Fermi momentum of the system which is related to the carrier density $n = k_F^3/3\pi^2$. Units of $\hbar = 1 = c$ are used.

The main purpose is to examine the pair binding energy, ω, as a function of the carrier density, $n(k_F)$, the cut-off energy, ω_c, and the momentum of the pair, q.

We find that in a one-dimensional system, the binding energy of a pair as a function of momentum, has two relative maxima; the usual one at $q = 0$; and a new maximum at a value of $q > 2k_F$. Thus, pairs having $q > 2k_F$ might be stable, or metastable, depending on k_F. For $k_F < k_m$, both maxima are in one range of q, thus pairs $q > 2k_F$ would be metastable. However, for $k_m \leq k_F \leq k_M$, two maxima are in separate range of q, so that pairs $q > 2k_F$ might be stable. Here the two important characteristic densities are $k_m = (m\,\omega_c)^{1/2}/2$ and $k_M = mV_{BCS}/2\pi$, where V_{BCS} is the BCS coupling constant in one dimension. For this, the cut-off energy should be $\omega_c \leq (\pi k_M)^2/2m$.

For a three-dimensional system, we find that pairs with $q > 2k_F$ can have finite binding energies only when $\omega_c \geq K_o^2/2m$, where $K_o = 2\pi^2/mV_{BCS}$. There exists an upper bound q_c such that only pairs with $q < q_c$ are bound. The upper bound is found to be independent of the carrier density, and depends on only the cut-off energy and the coupling constant. It is given by $q_c = \omega_c/v_A$, where $v_A = K_A/m$, and $K_A = K_o/\ln 2$. The binding energy in this case is a monotonic decreasing function of momentum with the zero-momentum pairs being most strongly bound.

The starting point is the binding energy equation [15],

$$1 = V_{BCS}\sum_k 1/(\omega + \epsilon_1 + \epsilon_2)$$

where $\quad \epsilon_{1,2} = (\tfrac{1}{2}q \pm k)^2/2m - k_F^2/m,$

with $\quad k_F < |\tfrac{1}{2}q \pm k| < K_F = (2m\,\omega_c + k_F^2)^{1/2}$

To carry out the integration of Eq. (1), it is convenient to consider six separate regions on the k_F - q plane. These six regions are shown in Fig. 11.

In one dimension, we find, by integrating Eq. (1),

$$1/K_5 = F_1 = (1/2K_6)\ \ln\{(K_1 - K_6)(k_2 + K_6)/K_1 + K_6)(k_2 - K_6)\}$$

for $q \leq K_F - k_F$, $2k_F$, $1/K_5 = F_2 = 0$, for $K_F - k_F \leq q \leq 2k_F$,

$$1/K = F_3 = (1/K_7)\ \tan^{-1}\{(K_1/K_7) - \tan^{-1}(k_1/K_7) - \tan^{-1}(k_2/K_7)\},$$

for $2k_F \leq q \leq K_F - k_F$,

$$1/K_5 = F_4 = (1/K_7)\ \tan^{-1}(-k_1/K_7), \text{ for } K_F - k_F \leq q \leq K_F + k_F$$

$$1/K_5 = F_5 = (1/K_7)\ \tan^{-1}(K_1/K_7), \text{ for } K_F + k_F \leq q \leq 2k_F,$$

$$1/K_5 = F_6 = 0 \qquad \text{for } 2K_F \leq q$$

where $K_5 = mV_{BCS}/\pi$, $K_1 = K_F - q/2$

$$k_1 = k_F - q/2,\ k_2 = k_F + q/2,$$

$$K_6 = k_F^2 - m\,\omega - q^2/4 = -K_7^2.$$

By studying the functions F_i, one finds the desired objectives. These results are illustrated in Fig. 11. For the case of $q = 0$, we find that the binding energy of a zero-momentum pair decreases as carrier density increases. On the other hand, we find that the binding energy in region 4 increases a q increases for given k_F and ω_c,

$$(d\omega/dq)_{k_F,\omega_c} > 0, \text{ for } k_m \leq k_F \leq k_M,$$

near $q \geq 2k_F$, but in region 5, for all q,

$$(d\omega/dq)_{k_F,\omega_c} < 0$$

Thus, the pairs which have some value of q between $2k_F$ and $2K_F$ have a relative maximum binding energy. The binding energy of a pair in region 4 is found to decrease with respect to k_F, and to vanish at $k_F = K_M = K_5/2$ as shown in Fig. 11. Now the condition for having two regions of q where pairs have finite binding energies is simply given as $K_F - k_F \leq 2k_F$, or $k_F \geq k_m = (m\omega_c)^{1/2}/2$.

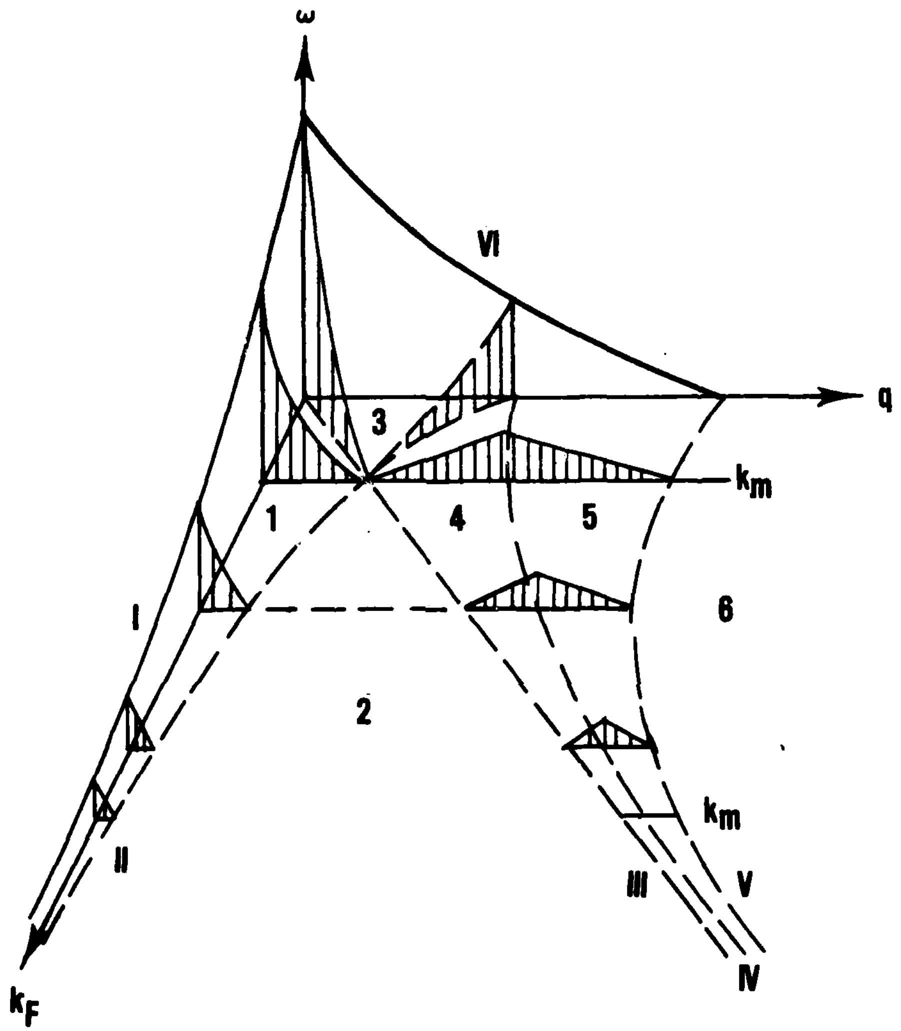

Fig. 11. The binding energy of a pair of carriers in a one-dimensional system as a function of the carrier density, $k_F(n)$, and the momentum of the pair, q. The curves labeled I and VI are the binding energies in the limit $k_F = 0$, respectively. The curves labeled II, III, IV, and V are $q = K_F - k_F$, $q = 2k_F$, $q = K_F + k_F$, and $q = 2K_F$, respectively. The regions 1, 2, 3, 4, 5, and 6 are discussed in text.

For the three-dimensional system, we carry out the same calculations as in the one-dimensional case. The results are shown in Fig. 12. One can get the corresponding functions F_i in the six separate regions of the k_F-q plane. The condition for a pair of $q \geq 2k_F$ having a finite binding energy is determined from the corresponding function F_3 in the limit $\omega \to 0$ and $k_F \to 0$,

$$F_3 = 2K_o = x^{1/2} = \tfrac{1}{2}q - \tfrac{1}{2}\pi q - (x/q)\ \ln\{1 - q(x^{1/2} - \tfrac{1}{2}q)/x\},$$

where $x = 2m\ \omega_c$.

This equation has a solution for q only when $\omega_c \geq K_o^2/2m$.

For pairs with $q \leq 2k_F$, the upper bound of q for pairs having finite binding energies is determined from the corresponding functions F_1 and F_2 in the limit $\omega \to 0$. We find

$$F_1 = 2K_o = K_F - k_F - q - (x/q)\ \ln(1 - qK_1/x)$$

$$+ k_o\ \ln\{(x - qK_1)(k_2 + k_o)^2/(qk_2)(k_1 + k_o)^2\}$$

$$F_2 = 2K_o = (x/q)\ \ln 2,$$

where $k_o = (k_F^2 - q^2/4)^{1/2}$

From the above equation, we find the upper bound of q for pairs having finite binding energies is

$q \leq q_1$ for $k_F \leq K_A - q_c$ and $q \leq q_c$ for $k_F \geq K_A - q_c$

where q_1 is a solution from F_1 as shown in Fig. 12.

In this case, for given k_F, the pair has a finite binding energy in one region $q < q_1, q_3, q_4, q_5, q_c$, where q_i are determined from the corresponding functions F_i in the limit $\omega \to 0$. All q_i are less than q_c. In particular, we find that for given k_F and ω_c the binding energy of a pair decreases as q increases as shown in Fig. 2. The binding energy goes to zero as q reaches the upper bound with a zero slope with respect to q [16].

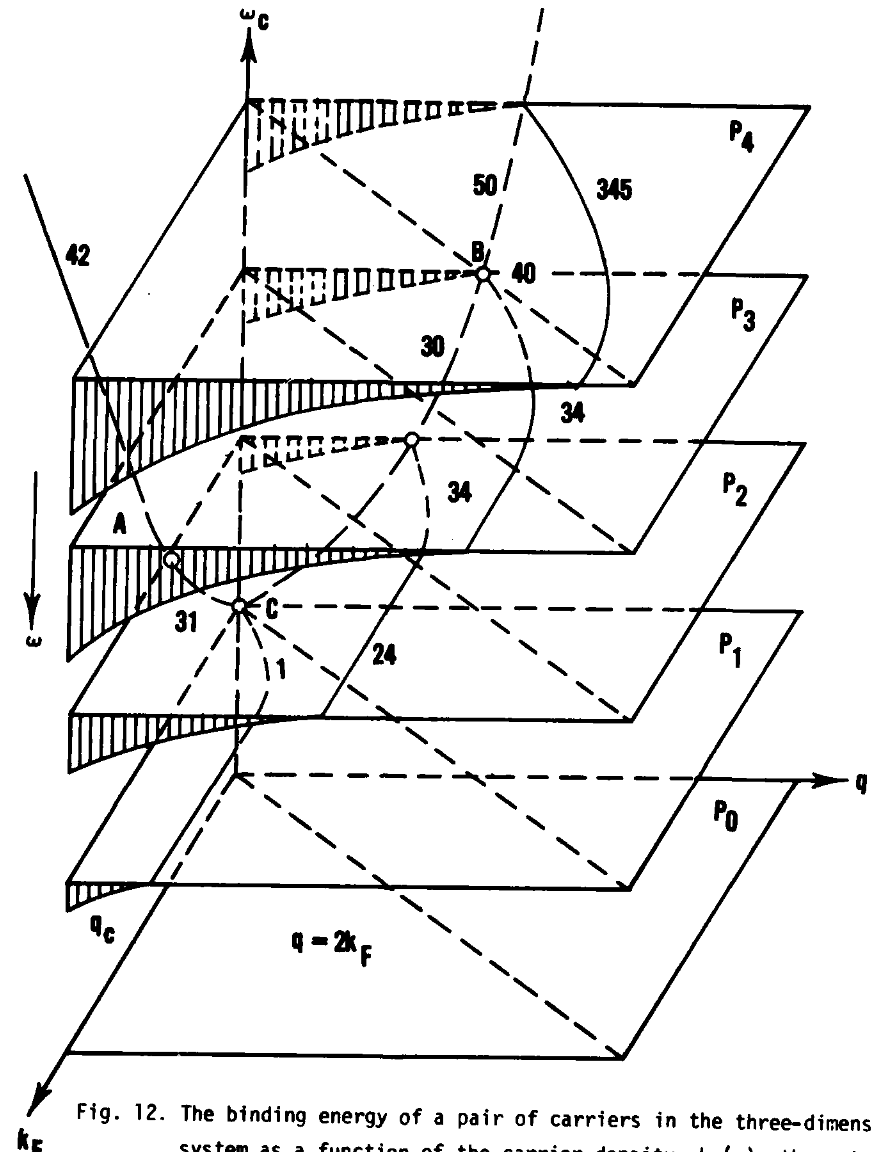

Fig. 12. The binding energy of a pair of carriers in the three-dimensional system as a function of the carrier density, $k_F(n)$, the cut-off energy, ω_c, and the pair momentum, q. The planes labeled P_o, P_1, P_3, and P_4, are the k_F - q planes with $\omega_c = 0$, $\omega_c = K_o^2/2m$ (C), $\omega_c = K_A v_A$ (A), ω_c = B such that the region 4 becomes a single point at $k_F = 0$, and ω_c being larger than others, respectively. The curves labeled ij are determined from the corresponding functions F_i and F_j discussed in the text. The curves of 30 and 50 are determined from the corresponding functions F_3 and F_5 in the limit $\omega \to o$ and $k_F \to o$, respectively. The point 40 is a single point where F_3, F_4, and F_5 meet at $k_F = 0$. The planes above p_1 can have regions where pairs of $q \geq 2k_F$ are allowed.

We conclude that in a one-dimensional system a pair of carriers with momentum $q > 2k_F$ can be locally stable, or metastable. The material parameters required to permit the occurrence of such pairs appear to be not very restrictive. Therefore, these pairs would play a role in quasi-one dimensional materials such as organic superconductors and superconducting polymers. Furthermore, it is very interesting to note that filamentary structures have been observed in high pressure quenched CdS[17], Cu Cl, and CuBr[18] under high pressure, which are suggestive of quasi-one dimensional behavior.

However, in the three-dimensional case, the condition to have pairs of momentum $q \geq 2k_F$, namely $\omega_c \geq K_0^2/2m$, is unlikely to be met for ordinary metals where the cut-off energy is determined by phonon frequencies. On the other hand, for degenerate semiconductors, the Fermi momentum may be sufficiently small so that the required condition might be satisfied.

For two component carriers, such as degenerate semiconductors[12], we can carry out a similar calculation. The algebra becomes more complicated, but we can make a comment about q in this case. We expect that the pairs with $q = k_{2F} - k_{1F}$ should be the most important, where k_{2F} and k_{1F} are the Fermi momenta of the two carriers, respectively. The formal results would be similar to those of the one component system. If one considers the three-dimensional upper bound limit $q \leq q_c$, then $q = (m^{\frac{1}{2}} - m^{\frac{1}{2}})(2\varepsilon_F) \leq q_c$. In other words, one cannot have a pair of carriers whose mass difference is very large.

The true ground state of a system having two component carriers appears to be a state of pairs of q and -q. In other words, if pairs of momentum q are occupied, then so are those of -q, so that the Block theorem would be satisfied. If this is the case, we expect several interesting results[14]. In particular, the fluxoid quantization will be half of the normal value, $\phi = hc/4e = 1.03 \times 10^{-7}$ gauss-cm^2, and the Josephson frequency relation becomes doubled, $h\nu = 4eV$. A model of two component pairings appears to be so rich that an extensive study is desirable[16].

SECTION V

CONCLUSIONS

Contributions to this exciting and potentially technological important field of research that were made on the LDF program are summarized in the following publications:

1) Donor-Acceptor Recombination Spectra in Cu Cl, D. C. Reynolds, R. J. Almassy and C. W. Litton, Phys. Rev. Letters, 44, 204 (1980).

2) Magnetic Properties of Pressure Quenched CdS, S. B. Nam, Y. Chung and D. C. Reynolds, Unpublished.

3) Pairing of Holes in Semiconductors, S. B. Nam, Proc. 16th Int. Conf. Low Temp. Phys. UCLA (Aug 1981).

4) Lecture notes given at the 3rd US Army Symposium on High Pressure Phenomena, Renssalaerville, New York (16-19 June 1981), S. B. Nam.

5) Stability of Finite Momentum Pairs in Degenerate Fermi Systems, S. B. Nam and D. W. Allender, Submitted to Phys. Rev. Letters.

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16. S. B. Nam and D. W. Allender, (unpublished).

17. S. B. Nam, Y. Chung, and D. C. Reynolds, (unpublished) have oberserved the filamentary structures in high pressure quenched CdS.

18. S. Ves, D. Gloetzel, M. Cardona, and H. Overhof, preprint.

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